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Performance, materials and coating technologies of thermochromic thin films on smart windows

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ABSTRACT

A significant amount of energy is consumed to maintain thermal comfort in buildings, a huge portion of which is lost through windows. Smart coating, thin films with spectrally selective properties on the surface of glass, is the innovative solution to the problem. Thermochromic smart windows change their color and optical properties in response to temperature variations. The performance, materials, coating technologies and energy modeling of thermochromic windows are reviewed in the present study. The effect of doping vanadium dioxide (VO_2) coatings with different dopants such as tungsten, fluorine, gold nanoparticles and etc. is elaborated. Various deposition techniques, specifically hybrid chemical vapor deposition (AA/APCVD) and physical vapor deposition (PVD) methods are elucidated. Different dopants and techniques show different results on metal to semiconductor transition (MST) and the critical temperature. The “change in visible and infra-red transmission and reflectance” is the touchstone of performance for the different afforded chromogenic intelligent windows.

Contents

1. Introduction

A significant amount of energy is consumed for maintaining thermal comfort in buildings. The energy used to maintain thermal comfort in buildings is mostly exploited to keep HVAC devices running. The building energy consumption in developed countries accounts for 20–40% of the total energy use. About 41% of primary energy the U.S. (as the second largest consumer of world energy representing 19% of global consumption), consumed in 2010 was for buildings sector. Consequently, this amount accounted for 7% of global energy use in 2010. Approximately 60% of all used energy in building sector was consumed for space heating, space cooling, lighting and ventilation in 2010 [1]. Buildings in China, as the largest consumer of world energy, consumed 26% of total primary energy in 2006; the figure is anticipated to rise to more than 30% by 2020 [2]. The building energy consumption is even more dominant in hot and humid regions, using one-third to half of the electricity produced in some countries [3–5].

In addition, building sector was the culprit of around 40%, 18% and 8% of energy-related carbon dioxide emissions in 2010 for the US, China and worldwide, respectively [1,6]. Therefore, energy saving measures should be taken in order to reduce buildings energy losses and CO_2 emissions.

There are two approaches in building energy saving strategies, the active strategies and the passive ones. Improving HVAC

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Nomenclature

TC	Thermochromic
EC	Electrochromic
TCW	Thermochromic window
ECW	Electrochromic window
SPD	Suspended particle device
MST	Metal to semiconductor transition
ΔT	Change in transmittance
T_t	Transition temperature (critical temperature)
PVD	Physical vapor deposition
CVD	Chemical vapor deposition
APCVD	Atmospheric pressure chemical vapor deposition
AACVD	Aerosol assisted chemical vapor deposition
ΔR	Change in reflectance

systems and building lighting can actively increase the building's energy efficiency, whereas measures amending the properties and thermal performance of building envelopes such as adding thermal insulation to wall, using cool coatings on roofs and coated window glazing are among the passive methods. Any building element, such as wall, roof and fenestration which separates the indoor from outdoor is called building envelope [7–10].

Windows are known as one of the most energy inefficient components of buildings [11]. Preventing these losses by improving the windows thermal performance will result in reduced electricity costs and less greenhouse gas emissions. While controlling transmitted Infrared (IR) radiation, an ideal window should be capable of sufficient transmission of visible light [12]. The most significant parameters influencing the heat transfer through windows include outdoor conditions, shading, building orientation, type and area of window, glass properties and glazing characteristics [13]. Improving glazing characteristics of windows such as thermal transmittance and solar parameters is the most important criterion to be considered in building windows standards [14]. Several international standards have been published to evaluate the performance of windows and glasses in building in order to achieve minimum requirement by considering energy performance improvement of building. ISO 10291:1994 [15], ISO 12567:2005 [16,17], ISO 9050:2003 [18], and ISO 14438:2002 [19] are the examples of such standards.

Based on international standard (ISO 9050) [18], light transmittance, solar direct transmittance, total solar energy transmittance, ultraviolet transmittance and related glazing factors are the essential parameters for determining the light and energy performance of glazing in building. Some studies have been done based on this standard (or its European equivalent EN 410) [20] in order to determine the optical properties of coated glass products [21], modeling the solar energy transmittance of windows by considering to the angular behavior, and calculate the solar control parameters [22].

Generally, international standards specify the criteria and the essential characteristics to be considered worldwide. International standards can apply directly or modify based on the local conditions. There are many international and local standards related to the energy and lighting performance of windows, some of which are tabulated in Table 1.

The thermal dynamics and lighting potential of glazing should be considered in building energy calculations. Energy efficiency in building envelopes is generally calculated based on the ratio of the temperature difference across a building compartment and the heat flux (R-value) or the rate of heat transfer through a building element at certain conditions (U-factor). In cold climates, low U-factors or high R-values prevent heat from escaping from buildings, and in hot climates, they prevent heat from entering buildings [23,24].

2. Smart windows

Smart windows, defined as the type of windows that partially block the unwanted solar radiation, can help building to maintain higher energy performance levels. The energy performance can be improved by increasing heat gain in cold weather and decreasing it in hot weather by adopting windows' radiative and thermal properties dynamically [25]. Adding controllable absorbing layer on the surface of the glass can change the optical properties of the glass by controlling the incident solar heat flux [26]. Therefore, smart windows lead to reduced HVAC energy consumption and size and electric demand of the building [11,27,28].

There is a wide range of modern intelligent glazing options for energy saving purposes including Low-e coatings [29,30], micro blinds, dielectric/metal/dielectric (D/M/D) films [31,32], and switchable reflective devices including electrochromic windows (ECW) [33–35], gasochromic windows [36], liquid crystal glazing [11], Suspended-Particle Devices (SPD) [37] and thermochromic windows (TCW).

Low emissivity (low-E) coatings are spectrally selective films that are aimed to let the visible light pass through and block the IR and UV wavelengths which generally create heat [10]. Because of its high IR-reflectance, this type of glazing has been developed greatly, and many have studied their different properties during the last two decades [30,38–40]. Typically, there are two types of low-e coatings, the tin oxide based hard coating and the silver based soft coating with higher IR reflectance and lower transmittance than the other one. However, the visible transmittance of hard coatings can boost up with anti-reflecting property of silicon dioxide [29].

D/M/D films on glass exhibit great energy saving effects by reflecting the IR radiation by their reflective metal film and transmitting visible and near IR radiation through the two antireflective dielectric coatings [41]. Design, fabrication and properties of D/M/D films have been studied thoroughly by many researchers focusing on the optimization [31,32,42–45]. Beside the optimized performance, cost of these films in terms of their material and the fabrication technique is also important [41].

The switchable reflective devices (also called dynamic tintable windows) are categorized in to passive and active systems. In passive devices, the switching process is activated automatically in accordance with the environmental conditions. This environmental factor can be light in case of photochromic windows; or temperature and heat in thermochromic windows (TCW). Alternatively, the active systems require an external triggering mechanism to perform the modulation. For instance, electricity is the actuating signal in electrochromic windows (ECW). The active switchable glazing systems offer supplementary options compared to the passive systems whereas their dependency on power supply and wiring should be reckoned with as a drawback. Chromic materials, liquid crystals, and suspended particle windows are the three most common active-controlled intelligent windows [11]. The latter two share the disadvantage of their dependency on an electric field to be maintained when a transparent mode is desired; resulting in excessive electricity consumption. This is not the case in EC glazing that wants electricity only for transition [46]. However, chromic materials are classified into four types: electrochromic (EC), gasochromic, photochromic and thermochromic (TC). The first two belong to active glazing, responding to electricity and hydrogen

gas, respectively, as a function of solar irradiation [11,47]. Smart windows are apt to glazing the cooling load demanding buildings with large solar gain [48], though providing a see-through mode is a must in any application.

The EC effect which was first explained in 1969 is a characteristic of a device which varies its optical properties when an external voltage triggers the EC material. The EC device modulates its transmittance in visible and near IR when a low DC potential is applied [34,49].

It is usually consisted of several layers deposited on glass. The glass substrates are usually coated with transparent conducting films with natural colors-mostly tin oxide doped with either indium (ITO) or fluorine (FTO). The three major deposited layers cover the coated glass substrate as follows: *The Electrochromic film* (cathodic electro-active layer with reversible transmittance modulation characteristic) which gets a darker color when the external circuit transfers electrons into the EC lattice to compensate for the positive ions injected from the adjacent ion storage layer; *Ion conductor* (ion conducting electrolyte); and *Ion storage layer* (anodic electro-active layer) that becomes darker while releasing positive ions [33,34,50–52].

The electro-active layers (also named electrochromics) switch between their oxidized and reduced forms causing variations in their optical properties and colors as well. Ideally, it is desired that electrochromics act more reflective rather than absorptive in their colored state compared with their bleached mode [49].

EC windows should provide daylight while acting as a barrier to heat. Obviously, this type of window is not capable of providing both effects simultaneously [35]. The EC function can be controlled by thermal load, temperature and sunlight. The latter is stated to be the best governing parameter, especially from the comfort point of view [53–56]. All the more, self-powered EC windows are also developed using semitransparent PV cells, which provide the required activating electricity [57–65].

The function of gasochromic devices is also based on electrochromism in EC windows. The main difference is that instead of DC voltage, a hydrogen gas (H_2) is applied to switch between colored and bleached states. Compared to their counterpart, gasochromic devices are cheaper and simpler because only one EC layer is enough and the ion conductor and storage layers are not needed anymore. Although, gasochromic devices exhibit some merits such as better transmittance modulation, lower required voltage, staying lucid in the swap period, and adjustability of any middle state between transparent and entirely opaque; only a few numbers of EC materials can be darkened by hydrogen. Furthermore, strict control of the gas exchange process is another issue [66].

Commonly used in wrist watches, LC technology is getting more popular as a means of protecting privacy in some interior applications such as bathrooms, conference halls and fitting rooms in stores. Two transparent conductor layers, on plastic films squeeze a thin liquid crystal layer, and the whole set is pressed between two layers of glass. Normally, the liquid crystal molecules are situated in random and unaligned orientations scattering light and cloaking the view to provide the interior space with privacy. When the power is switched on the two conductive layers provide

Table 1
Energy and lighting performance standards of windows.

Name	Description	Country
ASTM E−2141-06	Standard test methods for assessing the durability of absorptive electrochromic coatings on sealed insulating glass units	International [11]
ISO 9050:2003	Glass in building—determination of light transmittance, solar direct transmittance, total solar energy transmittance, ultraviolet transmittance and related glazing factors	International [22]
ISO 10291:1994	Glass in building—determination of steady-state *U* values (thermal transmittance) of multiple glazing—Guarded hot plate method	International
ISO 10292:1994	Glass in building—calculation of steady-state *U* values (thermal transmittance) of multiple glazing	International
ISO 10293:1997	Glass in building—determination of steady-state *U* values (thermal transmittance) of multiple glazing- Heat flow meter method	International
EN 1096-1:2012	Glass in building—coated glass—Part 1: definitions and classification	European
EN 1096-2:2012	Glass in building—coated glass—Part 2: requirements and test methods for class A, B and S coatings	European
EN 1096-3:2012	Glass in building—coated glass—Part 3: requirements and test methods for class C and D coatings	European
EN 1096-4:2004	Glass in building—coated glass—Part 4: evaluation of conformity/Product standard	European
EN ISO 14438:2002	Glass in building—determination of energy balance value—calculation method (ISO 14438:2002)	European
BS EN 14449-1:2005	Glass in building. Laminated glass and laminated safety glass. Evaluation of conformity/product standard	British
BS EN 14179-2:2005	Glass in building. Heat-soaked thermally-toughened soda lime silicate safety glass. Evaluation of conformity/product standard	British
BS EN 1748-1-2:2004	Glass in building. Special basic products. Borosilicate glasses. Evaluation of conformity. Product standard	British
BS EN 12337-2:2004	Glass in building—chemically strengthed soda lime silicate glass—evaluation of conformity/Product standard	British
BS EN 14178-2:2004	Glass in building—basic alkaline earth silicate glass products—evaluation of conformity/Product standard	British
BS EN 1096	Coated glass	British
BS EN 12898: 2001	Glass in building, determination of the emissivity	British
BS EN 410: 1998	Glass in building—determination of luminous and solar characteristics of glazing	British
BS EN 673: 1998	Glass in building: determination of thermal transmittance (value). Calculation method	British
BS EN ISO 12567	Thermal performance of windows and doors	British
BS EN ISO 14438:2002	Glass in building. Determination of energy balance value. Calculation method	British
ES ISO 12567-1:2012	Thermal performance of windows and door—determination of thermal transmittance by the hot box method—complete windows and doors	Ethiopian
ES ISO 12567-2:2012	Thermal performance of windows and door—determination of thermal transmittance by the hot box method—roof windows and other projecting windows	Ethiopian
ES ISO 14438:2012	Glass in building. Determination of energy balance value. Calculation method–calculation method	Ethiopian

Table 2
Comparison between different smart windows.

Smart windows	Activation	Colour	Advantages	Disadvantages	Thermal performance	Optical performance	Application
Photochromic	Light	Bleach	No activation electricity, No foggy effect, Automatic	Manufacturing difficulties for large sizes, limited application, Cannot reduce heat gain, More darker in the winter than the summer		UV protector, darken and lighten at sunlight and dusk	Sunglasses, Supramolecular chemistry, data storage
TC	Heat	Colored	High energy saving, No activation electricity	No outside visibility, manufacturing difficulties for large sizes	Reflecting heat gain	Reflecting infrared light	Duracell battery state indicators, Thermochromic paints, Thermochromic papers are used for thermal printers, thermochromism polymer
EC	Voltage/ current	Colored	Energy saving	Activation electricity is needed	Control the amount of heat	Reversibly changing color when a burst of charge is applied, control the amount of light	Electrochromic devices such as windows and smart glasses, Automobile industry
Liquid Crystal	Voltage	Bleach	Control privacy	No energy saving, No outside visibility, Activation electricity is needed	High heat gain	Transmit incident light	Electrooptical devices, hyperspectral imaging
Suspended Particle	Current	Bleach	Instantaneous control of light, Outside visibility, Have wide range of transmittance	Limited in size, Activation electricity is needed	Energy saving	UV protector, Reduction of infrared light,	Polaroid camera, Windows

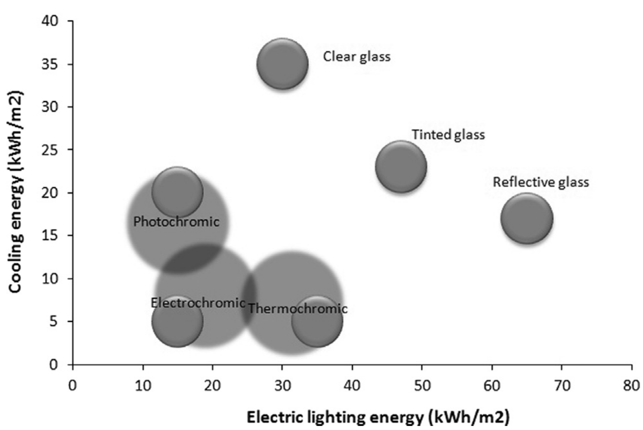


Fig. 1. Comparison of electric lighting energy and cooling energy between different glazing types [24].

an electric field via their electrodes. The field causes the crystal molecules to be positioned in an aligned direction causing a change in transmittance [67,68]. The LC technology suffers from the disadvantage of high power demand in transparent mode, resulting in an electricity usage of 5–20 W/m^2. These devices have problems, in long term UV stability and high cost disadvantages as well [11]. The technology using liquid crystals in intelligent windows is called Polymer dispersed liquid crystals (PDLC).

SPDs have many things in common with LC devices: they are both fast in switching between phases, high electricity consumptive and dependent on an electric field. They consist of the liquid like active layer formed by adsorbing dipole needle-shaped or spherical particles (molecular particles), i.e. mostly polyhalide, suspended in an organic fluid or gel sandwiched between two sheets of glass coated with transparent conductive films. Normally, the device is in the dark reflective state because of the random pattern of the active layer's light absorbing particles. When the electric field is applied, the particles will align resulting in the clear transmissive state. As soon as the power turns off the device switches to its dark state. Typically, the transmission of SPDs varies between 0.79–0.49 and 0.50–0.04, with 100 to 200 ms switching time and 65–220 V AC requirements [11]. The critical comparison between different smart windows is summarized in Table 2.

Shown in Fig. 1, clear glass, tinted glass, reflective glass and three chromogenic fenestration technologies are compared regarding to their cooling and electric lighting energy. As it is observed EC and TC windows demand the lowest cooling energy; and as previously reported ECWs require less energy for lighting than TCWs [69]. However, the necessity of wiring in EC glazing and the better ability of TCWs to maintain the visible transmission (when doped properly) [70] besides their simple structure [71] have given TCWs a cutting edge as a low-priced [72] alternative to the other counterparts.

Different technologies such as electrochromic, gasochromic, liquid crystal and suspended particle devices have been widely reviewed neglecting the TCWs [11,37,46,73]. As a result, there was a need to review thermochromic windows comprehensively. The following sections address the application of TC thin films in fenestration. Part 3 introduces thermochromism, TCWs, their structure, and their performance. Part 4 discusses TC materials, the dopants and the nanoparticles. In part 5 thin film deposition and fabrication techniques are addressed. In part 6 the energy modelings done on TCW are discussed. And lastly, in part 7 there will be a conclusion covering the whole papers reviewed.

3. Thermochromic windows (TCW)

In the first glance, the word “Thermochromic” might seem strange. But the word originates from the Greek roots: “Thermos” meaning warm or hot; and “Chroma” which means color. Generally,



Fig. 2. Sequential color switching of a thermochromic laminated glass [4].

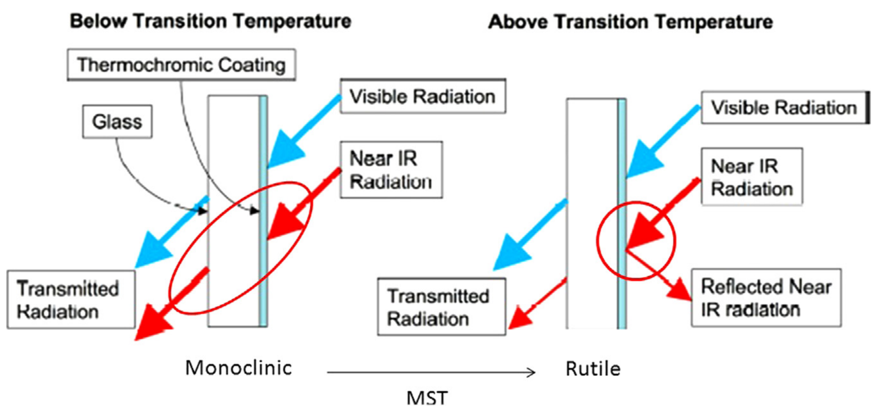


Fig.3. Schematic representation of thermochromic materials applied as an intelligent windows coating [77].

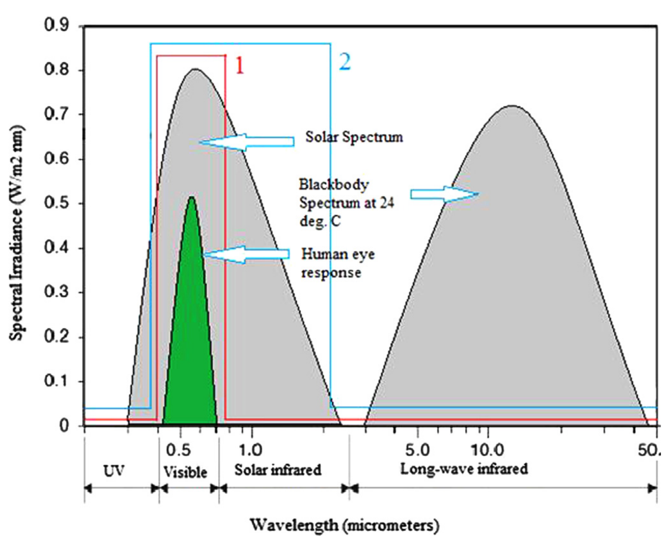


Fig. 4. The spectral transmittance of perfect TCW in cold and hot weather conditions (adopted from [81]).

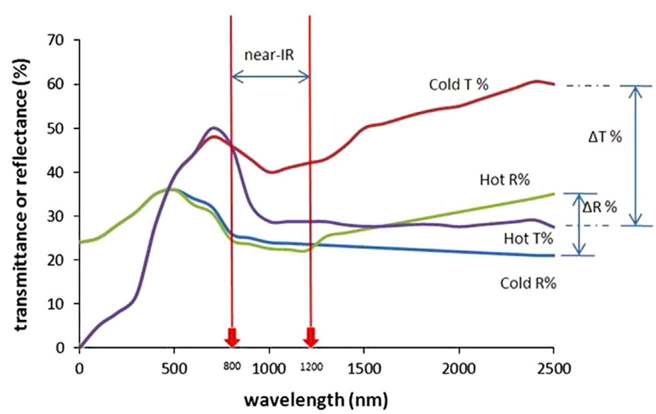


Fig. 5. Typical transmittance change (ΔT) and reflectance change (ΔR) of thermochromic films through MST (adapted from [91]).

Table 3
The Ideal optical performance of thermochromic windows (adapted from [91]).

State	Monoclinic/cold ($T < T_t$)		Rutile/hot ($T > T_t$)	
Wavelength	Visible (%)	NIR (%)	Visible (%)	NIR (%)
Transmittance (T)	60–65	80	60–65	15
Reflectance (R)	17	12	17	77

thermochromic (TC) materials change color in response to temperature variations. Thermochromic window, an example of which is shown in Fig. 2, is a type of glass with TC materials that can reduce the energy demand of buildings by changing the device's reflectance and transmission properties and reducing the unwanted solar energy gain [74,75].

The TC thin film is initially in its monoclinic state (cold state) at lower temperatures (usually room temperature). Monoclinic materials behave as semiconductors, less reflective especially in near-IR (NIR) radiation. As the temperature becomes higher than a certain point, the TC material changes its nature from monoclinic to rutile state. This phenomenon is called metal to semiconductor transition (MST). In rutile state (hot state) the material acts like a semi-metal, reflecting a wide range of solar radiation [76] (Fig. 3).

As illustrated in Fig. 4, the majority of heat gain in solar spectrum takes place at NIR range (800–1200 nm) [78–80].

The red line (line 1) indicates the transmittance of perfect TCW in cold state. Visible light should be transmitted and near infrared radiation should be reflected. Long-wave radiation is also reflected back to indoor. This transmittance approach leads to reduction of

solar heat gain and is apt in nearly all climates. The blue line (line 2) indicates the transmittance of perfect TCW in hot state. Visible and near infrared radiation are transmitted, while long-wave infrared is reflected to inside. This transmittance mode is suitable in low temperature climates where solar heat gain is desired. Therefore, in high temperatures TCWs reduce NIR and far-IR transmittance, while in low temperatures they allow these parts of solar radiation to pass [82] (Fig. 5).The MST is fully reversible, co-occurred with large variations in electrical and optical properties in NIR range [83]. Transition temperature of pure vanadium dioxide as the most common TC material in TCWs is about 68 °C which is considered a high temperature. In order to make this type of glazing feasible, the MST temperature (T_t) should decrease to near the ambient temperature. Doping metal ions into the lattice of TC materials can alter T_t [84,85]. The size and charge [84,86,87] of dopant ion, film's strain [88,89] as well as the variations in electron carrier density are the determinant factors prevailing on the fall or rise of T_t [90].

The ideal spectral behavior of TCWs is presented in Table 3. The visible transmission and reflectance should be equal in both sides of transition while the infra-red variations are from 0% to 65%. The change in transmittance ($\Delta T\%$) and reflectance ($\Delta R\%$) can be formulated in Eqs. (1) and (2) [92]:

$$\Delta T\% = (T_h - T_c) \times 100 \qquad (1)$$

$$\Delta R\% = (R_h - R_c) \times 100 \qquad (2)$$

where T_h is transmittance at hot state, T_c is transmittance at cold state, R_h is reflectance at hot state and R_c is reflectance at cold state.

The most critical weakness of VO_2 coatings is their low transmittance in visible range (T_{vis}). Many studies have reported values between 40% and 50%, which is well below the acceptable value of 60% [93,94]. The reported values of transmittance and reflectance measured before and after T_t for VO_2 coatings are presented in Table 4.

Besides low luminance visibility, low energy-saving efficiency also makes application of VO_2 coatings limited. The change in transmittance before and after T_t at 2500 nm known as the switching efficiency (η_T) is the benchmark of energy-saving efficiency. This value is influenced by doping [107,108], microstructure [80,95,109–111], and film thickness [80,88]. The most paramount factor among them is film thickness that affects switching efficiency most significantly. However, increasing the film thickness has an adverse effect on T_{vis}. As it is observed in Table 4, the ideal film thickness is between 40 and 80 nm. Choosing the most suitable dopant (for reducing T_t and improving T_{vis}), the most appropriate coating technology (to acquire the optimum thickness and sufficient TC transition), adding efficient anti reflecting coating (to increase T_{vis}) and reducing the coating costs are the crucial steps to overcome the limited application of TWCs. In the following sections these factors will be discussed.

4. Thermochromic materials and dopants

Comparatively, almost all inorganic materials exhibit color change with temperature. Electronic properties of such materials at different temperatures cause this thermochromic effect. Though, some TC materials exhibit more drastic color and property changes with temperature. Some of the most renowned TC materials and their corresponding transition temperature are introduced in Table 5.

The TC materials for glazing purposes, their properties and fabrication are not new in glazing industry, having been studied by the early 1970s [115,116]. The most promising TC material for windows is vanadium dioxide (VO_2). It is known to be in four polymorphic forms: monoclinic VO_2(M) and rutile VO_2(R) and two metastable forms VO_2(A) and VO_2(B) by monoclinic to rutile transition temperature of 68 °C [117]. VO_2 TCWs suffer from low luminous transmittance, the drawback which could be solved by fluorination [118] or applying SiO_2 anti-reflective (AR) coating [82,119]. Using ZrO_2 coating with its appropriate refractive index is reported to enhance the luminous transmittance while maintaining the TC switching [120]. The most popular materials used in TC coatings, and their corresponding effects are presented in Table 6.

Table 4
Transmittance and reflectance values reported for various VO_2 coatings before and after transition temperature.

Thermochromic coating	Below T_t (Cold)				Above T_t (Hot)				η_T (%)
	T_{vis} (%)	R_{vis} (%)	T_{IR}[1] (%)	R_{IR}[1] (%)	T_{vis} (%)	R_{vis} (%)	T_{IR}[1] (%)	R_{IR}[1] (%)	
[95]: 280 nm tungsten-vanadium co-sputtered thin films on glass substrates by magnetron sputtering, T_c=20 °C,T_h=70 °C	**41**	6	60	14	41	8	12	30	**48**
[96]: RF reactive sputtered VO_2 thin films, T_c=26 °C,T_h=90 °C	**38**	–	67	–	48	–	10	–	**47**
[97]: deposited VO_2 thin films by CVD	**78**	–	–	–	74	–	–	–	
[98]: sputter deposited VO_2 thin films, T_c=20 °C,T_h=80 °C	**38**	–	72	–	44	–	10	–	**62**
[99]: RF reactive sputtered VO_2 thin films, T_c=20 °C,T_h=90 °C	–	–	59	–	–	–	5	–	**54**
[100]: RF sputtered CeO_2–VO_2 bilayers on SiO_2 substrates, T_c=25 °C,T_h=100 °C	**37**	24	59	25	20	15	3	43	**56**
[101]: 50 nm VO_2 thin films by the sol–gel process	**20**	–	60	–	35	–	5	–	**55**
[102]: VO_2 films produced by reactive e-beam evaporation	**48**	–	–	–	–	–	–	–	–
[103]: 70 nm deposited VO_2 films by APCVD, T_c=25 °C,T_h=65 °C	–	–	19[2]	–	–	–	11[2]	–	**18[2]**
[104]: 40 nm ZnO-doped VO_2 thin films	**60**	38	85	10	65	32	32	30	**53**
[105]: VO_2 thin films sputtered onto corning glass, T_c=25 °C,T_h=100 °C	**38**	–	–	–	32	–	–	–	–
[72]: 50 nm VO_2 thin films, T_c=22 °C,T_h=100 °C	**50**	42	76	20	55	39	20	41	**56**
[106]: RF sputtered VO_2 thin films with anti reflecting coating, T_c=20 °C,T_h=90 °C	**55**	–	52[3]	–	50	–	33[3]	–	**19[3]**
[76]: • 80 nm thick VO_2 films prepared by APCVD, T_c=25 °C,T_h=80 °C	**65**	20	80	10	65	20	50	13	**30**
• 80 nm thick Tungsten–doped VO_2 films prepared by APCVD, T_c=25 °C,T_h=40 °C	**55**	30	64	14	55	28	28	30	**36**

[1]: Measured at 2500 nm wavelength
[2]: Measured at 1500 nm wavelength
[3]: Measured at 1000 nm wavelength

T_{vis}: Visible transmittance; T_{IR}: Infra-red transmittance
R_{vis}: Visible reflectance; R_{IR}: Infra-red reflectance

Table 5
Thermochromic materials.

TC material	T_t (°C)	Cold state color	Hot state color	Reason of transition
Cuprous mercury iodide (Cu_2HgI_4) [112]	55	Bright red	Dark brown	Cu(I)–Hg(II) charge transfer
Silver mercury iodide (Ag_2HgI_4) [112]	47–51	Yellow	Orange	Cu(I)–Hg(II) charge transfer
Mercury(II) iodide	126	Red	Pale yellow	Reversible change transition
Bis (dimethylammonium) tetrachloronickelate [113]	110	Raspberry-red	Blue	
Bis (diethylammonium) tetrachlorocuprate [112]	52–53	Bright green	Yellow	Relaxation of the hydrogen bond an change of arrangement of the copper atom's d-orbitals d
Nickel sulfate	155	Green	Yellow	
Chromium(III) oxide: aluminium(III) oxide (1:9) [114]	400	Red	Grey	Changes in its crystal field
chromium-rich pyropes	80		Green	
normally reddish-purplish	80		Green	
titanium dioxide		White	Yellow	
zinc oxide		White	Yellow	
indium(III) oxide		Dark yellow	Yellow brown	
Lead(II) oxide		Dark yellow	Yellow brown	

Table 6
Effect of some materials on the thermochromic coatings.

Material	**Effect on MST**	$\boldsymbol{T_t}$	**Film color**
Pure VO_2 crystals	–	68 °C [117]	Brown/yellow [122]
Un-doped VO_2 films	–	50–66 °C [89]	Brown/yellow
Tungsten doping	23% ΔT at 2500 nm [108]	20 °C [76] 1.56 at% 25 °C [133] 2.7 mol%	Blue [76]
Gold nanoparticle	35–40% ΔT and 10% ΔR at 2500 nm [134]	15–20 °C [134]	Green/blue [124,125] Varies in different temperatures
Fluorine doping	15 % ΔT and 5 % ΔR [127]	60 °C [127] 25 °C [28]	Brown/yellow [127]
TiO_2	21.2% IR–ΔT and 84% Vis–ΔT [130] 5–10% ΔT at 2500 nm [128]	50–60 °C [128]	Brown [92,128]
CeO_2	5–10% ΔT at 2500 nm [128]	50–60 °C [128]	Brown/yellow[128]

Fluorine and tungsten-doped VO_2 are good choices for energy-saving windows [108,121]. However, tungsten (W) by reducing the T_t of VO_2 to the ideal temperature of 25 °C at 2 at% (lowering the T_t by 25 °C per dopant atomic percent incorporated) is the most effective dopant ion for VO_2 [76,122]. In another experiment, it is shown that a 2.7 mol% content of WO_3 has also made the film's T_t drop to room temperature [123].

Gold nanoparticles have been used as dopant in recent studies. It gives a pleasant green/blue color to the films and affects the MST and T_t. However, because of its high price, gold doping cannot be prevalent [124,125].

Fluorine doping of VO_2 films have been done by PVD techniques [28,121,126]. Incorporation of fluorine in the films using AACVD gave the films a lighter color but still the unpleasant yellow/brown color of un-doped film did not change [127].The changes in transmission (15%) and reflectance (5%) are less than those of tungsten-doped films. The key effect of fluorine is the better transmission in the visible range. In contrast to previous studies [28], it is reported that the transition temperature (~60 °C) did not change noticeably from the un-doped case [127].

Performed titanium dioxide (TiO_2) and cerium dioxide (CeO_2) nanoparticles have been also used in producing VO_2 films. By utilizing these photocatalytic nanoparticles, films with both photocatalytic and TC characteristics can be afforded. Through MST, the transmittance changes insignificantly (5–10%) at 2500 nm, while the reflectance changes about 30%. The nanoparticles used do not change the color of the film [128]. Moreover, CeO_2 can be used as a protective coating over VO_2 films to plunge the chemical deteriorations [129].

TiO_2 is used to fabricate double- (or multi-) layered VO_2 thin films. The anti-reflection feature of TiO_2 can enhance the visible transmittance up to 84% [130]. Deposition of platinum (Pt) on VO_2 films can improve the IR reflection while maintaining the TC characteristic. T_t has been also lowered by 9.3 °C to around 58 °C. Pt has depressed the visible transmittance which can be fortified by adding SiO_2 antireflection coating [131]. Earlier, SiO_2 was used to improve the luminous transmittance to 75% (in 700 nm) compared with 33% of plain VO_2 case. SiO_2 has also lowered T_t to 61 °C [132].

There are some materials which can be used as deposition precursor. The most common precursors are vanadium alkoxides [89,135–137] and oxovanadium reagents [138]. Vanadium chloride should react with a source of oxygen (such as methanol or ethanol) the product of which is V_2O_5; heating the product in a reducing atmosphere results in deposition of VO_2 [139]. Addition of tetraoctyl ammonium boromide (TOAB) as surfactant to the vanadium dioxide matrix can control the distribution, shape and size of gold nanoparticles. It is reported that surfactant TOAB can reduce T_t from 50–54 °C to 42–45 °C [140] and from 52 °C to 34 °C [134].

Surfactants are molecules, which can alter the structure of films due to their ability to affect the surface tension of liquids and deposition mechanism in hybrid CVD processes. Using surfactants can decrease T_t of VO_2 films [125,134,140].

Thermochromic coatings can also be used on surfaces other than window. For example, Karlessi et al. introduced TC coatings as buildings external surfaces to reduce the heating and cooling loads in winter and summer [109].

5. Thermochromic coating technologies

Deposition of TC thin films on different substrates by physical vapor deposition (PVD), sputtering and sol–gel [28,74,121,141–145] techniques was executed by the early 2000s. In particular, VO_2 as the most appropriate TC material had been deposited using sol–gel [135,146–148], sputtering [71,80,149], pulsed laser techniques and chemical vapor deposition methods (CVD). These methods have been widely reviewed in previous studies [87,94,150,151].

As it is mentioned before, doping VO_2 films with tungsten can enhance their TC property. The doping and production methods include sputtering and PVD [28,141,152] sol–gel [74,135,144,146–148], APCVD [76,79,89,122,153,154] and AACVD [155,156]. Despite the technological developments in surface engineering, until now, low visible light transmission, high transition temperatures, low durability, poor transition performance, high deposition costs and unpleasant visible colors did not let these techniques be marketable.

For instance, in an attempt to decrease T_t by doping Sn on VO_2 films using PVD, it was reported that the un-doped films showed much lower T_t [141]. Even the recent production of w-doped VO_2 and V_2O_5 films prepared by sputtering has not shown good switching performance [110]. There have been some efforts to optimize the TC switching of films by controlling the deposition conditions. The best results are 76% for ΔT and 75% for ΔR; though, T_t was still high [80].

Reactive sputtering is the most widely PVD method used to produce thermochromic thin films by means of ion beam sputtering [157], DC magnetron sputtering [152,158,159] and RF magnetron sputtering [78,160,161].

On the other hand, chemical vapor deposition (CVD) shows potential in manufacturing glasses in commercial scale. Specifically, atmospheric pressure chemical vapor deposition (APCVD) is well matched with float-glass mass production lines. The deposition rates of VO_2 films are noticeably fast in this method [76]. By the same token, the resulting physical properties such as durability and adhesion make this method more suitable [91]. There have been many researches investigating various CVD techniques and doping effects [76,79,122,162].

In a study conducted by Binions et al. [89] APCVD method was used to produce tungsten-doped VO_2 films by reaction of vanadyl acetylacetonate and tungsten hexachloride with oxygen. It is reported that tungsten doping causes a considerable drop in T_t as well as a great change in near infra-red optical properties [75]. The film thickness was also found to influence the transmission [89] and extent of TC switching [89,136]. The film thickness can be adjusted by changing the deposition time [134].

Using APCVD, TiO_2 on VO_2 on SiO_2-coated glass and VO_2 on TiO_2 on SiO_2-coated glass have been grown and compared. In both cases, the T_t did not change significantly. The $\Delta T\%$ in the first multilayer film was 92% noticeably more than that of the case of VO_2 over TiO_2 (71%). The two films showed $\Delta R\%$ of 55% and −55%, respectively [92]. In another study, two deposition methods were used: low pressure metal-organic CVD (MOCVD), and argon annealing of VO_2 (B) films by MOCVD. It was found that the film microstructure regulates the MST markedly [111].

Manning et al. [79,122] used water, vanadium and tungsten sources to prepare VO_2 thin films by CVD. The resulting films had the disappointing transmission of 11% to 40%. As previously suggested, the acceptable transmission level should be above 60% so that the window's optical properties can live up to the building's aesthetical and lighting standards [152].

Vernardou et al. [162] have studied the aftereffect of doping monoclinic VO_2 by atmospheric-pressure direct liquid injection metal-organic CVD (DLI-MOCVD). It was shown that T_t of tungsten-doped VO_2 drops from 60 °C to 35 °C. Aerosol assisted CVD (AACVD) is also another deposition process reducing V_2O_3 to V_2O_5 [155]. However, the AACVD techniques do not feature good mechanical properties and can be easily removed from the surfaces [163].

Hybrid atmospheric pressure and aerosol assisted (AA/APCVD) method can be used to prepare VO_2 thin films with reduced transition temperatures [124,134]. In this technique, the multifunctional feature of AACVD is mixed with the mechanical sturdiness of APCVD [124]. This method has been also used to prepare gold doped VO_2 films. Due to the surface plasmon resonance (SPR) bands, the gold nanoparticles change the color of films from unpleasant yellow/brown color to more appealing green/blue colors. In addition, it reduces the T_t and causes a surge in reflectance. The hybrid method results in more adherent films compared with AACVD films. As MST takes place, a 10% change in reflectance and 30–40% change in transmittance is observed at 2500 nm. The reason for this change may be the metallic nature of gold nanoparticles [140]. Hybrid AA/APCVD is also used to prepare VO_2 films by using a suspension of TiO_2 and CeO_2 [128].

Blackman et al. [76] used Water, vanadium chloride, and tungsten chloride for synthesizing tungsten-doped VO_2 thin films by APCVD. Among the different afforded un-doped films, the optical properties of which having been measured between 300 nm to 2500 nm wavelengths, the 80 nm-thick films showed the best performance with 60% transmission at 570 nm (visible range) and 35% change in transmission at 2500 nm (far infra-red range) through transition. Testing the tungsten doped films, the effect of different tungsten atomic percentages on reducing T_t has been evaluated. As it was previously reported [157], by increasing the tungsten content T_t changes (linearly [108]) approximately by -20 °C/at% until 3 at% after which the reduction will be pseudo linearly. In addition, the powdery yellow/brown color of films can change to more adhering, more transparent and bluer/greener films by adjusting the vanadium precursor to water ratio and increasing the tungsten content of films to more than 2.5 at%.

In choosing the deposition technique, several factors should be taken into mind including the limitations of the material to be deposited, substrate material, deposition rate, the cost of required equipments, scalability, environmental considerations and the desired film features such as thickness, micro structure, mechanical strength, and optical, thermal and thermochromic performance.

In the first glance, comparing the different VO_2 coating methods results in baffling outcomes. Compared to other techniques, PVD methods require expensive equipments and high vacuum pressure. In addition, they are time and energy consumptive and suffer from low film growth rates. To the contrary, PVD methods are more suitable for synthesizing ultra thin films, require lower temperatures, are more environmentally-friendly, compatible to a wider range of substrates and more convenient for developing multi-layer thin films [150,164]. On the other hand, CVD is believed to have the potential for producing glass in commercial scale, due to its compatibility to float-glass production line [165] and fast deposition rates [165,166]. However, PVD and CVD are considered as energy consuming techniques and are not

cost-efficient. Gao et al. reviewed solution processes for VO_2 films preparation and concluded that these methods are cheap, suitable for scaling up and easy to be utilized in practical applications. In contrast, the film characteristics such as thickness and microstructure are not precisely controllable by solution based methods [94].

To sum up, both PVD and CVD methods are suitable for experimental scale due to their scalability and superiority in terms of controlling process parameters and film features. However, they are restricted by the expensive machines and processes they require, while solution processes do not suffer from these drawbacks in industrial scale. There are two suggested approaches to these shortcomings: (1) to modify the PVD and CVD methods and to design more inexpensive equipments and coating processes (2) to improve the solution based methods so that the film features including visibility, micro structure, color, and film thickness can be adjusted by controlling the process parameters.

6. Energy modeling of thermochromic windows

There are various software tools which have been used in previous researches for window simulation including energy-10 [12], the window simulation tool Winsel [167], simulation tool SOLENE [168], self developed simulation software (SDS) based on the ASHRAE tables [13], DOE building energy simulation program [169], TRNSYS building energy simulation program [66] and simulation package Integrated ENergy Use Simulation (IENUS) [27]. Different smart windows configurations have been also simulated and modeled [167,170–175] for evaluating their energy saving effect and optical performance.

Based on theory, TCWs are capable of curtailing the buildings energy consumption by allowing visible day light, limiting undesired solar gain in the hot seasons and allowing favorable solar heat gain during the cold seasons. There a few number of studies which modeled and calculated the energy performance of TCWs. Saeli et al. modeled TCWs by energy plus software and demonstrated the technology's energy saving effectiveness both in lighting and ventilation. The total energy consumption reduced more for commercial windows (100% of wall area glazing) than the residential case (25% of wall area glazing). Since high temperature lets the window be longer in its rutile state, it was also discovered that the technology works best in cities with warmer climates [91]. They also compared TCWs with conventional glazing and showed the effectiveness of TC coating in saving energy [176].

In another study Xu et al. compared the cooling energy consumption of white glass and four Low-E glasses by using the software TRNSYS 16 and showed the best performance was attained by the double glass when the VO_2 films were coated on the inside surface of the outer pane with 85% energy saving compared to white glass. However, the heating energy consumption was the highest for TCWs [177]. The result of this study also shows that TCWs are more suitable for cooling demand climates.

To the contrary, Ye et al. evaluated the energy consumption of different windows by an energy analysis program "BuildingEnergy" and showed that VO_2 glazing has no apparent energy saving benefit and solar control advantage over conventional glazing. They concluded that, controlling the emissivity of the window is more beneficial than regulating the solar transmissivity. It was also concluded that, the energy saving effect of TCWs in summer is due to low transmittance of solar radiation and the higher absorptivity in the metal state results in higher energy consumptions which consequently makes the phase transition useless to the energy saving performance [151]. The inconsistency and scarcity of the studies in modeling the energy performance of TCWs emphasizes the necessity of more research in this field.

7. Conclusions

It's been decades since the time Vanadium dioxide thermochromic coating was reported, however, TCWs have not been commercialized due to shortcomings such as low luminance visibility, unattractive colors, low energy-saving efficiency and high coating costs. Nano technology, suitable dopants and adding efficient anti reflecting coating can reduce transition temperature (near room temperature) and improve visible transmittance (more than 60%). Appropriate and cost-efficient coating technologies provide optimum thickness (40–80 nm), sufficient thermochromic transition (more than 50%) and reduces the coating costs.

The coatings can be doped with different nanoparticles. Each dopant induces a special effect on the coating. Tungsten lowers the transition temperature, gold nanoparticles bring more pleasant film colors, fluorine increases the visible transmittance and titanium dioxide adds self-cleaning and mechanical strength to the films. The most common preparation methods are PVD, sol–gel techniques, and CVD. CVD is fast and suitable for mass production. AACVD and APCVD are the two most up-to-date deposition routes having multifunctional characteristics and mechanical strength, respectively. A prudent manner is to combine the qualities of both methods by employing hybrid AA/APCVD. To recapitulate, both PVD and CVD methods are suitable for experimental scale due to their scalability and superiority in terms of controlling process parameters and film features. However, they are restricted by the expensive machines and processes they require, while solution processes do not suffer from these drawbacks in industrial scale. There are two suggested approaches to these shortcomings: (1) to modify the PVD and CVD methods and to design more inexpensive equipments and coating processes (2) to improve the solution based methods so that the film features including visibility, micro structure, color, and film thickness can be adjusted by controlling the process parameters.

All in all, the major aims that must be reckoned with thermochromic glazing are to maximize the change in infra-red (predominantly 800–1200 nm) Reflectivity and transmission, tapering the transition temperature to near room temperature and maintaining the proper visible transmission to conserve the lighting energy. By the same token, the emissivity of the films should be modulated. Since the emissivity of the coatings are high in both monoclinic and rutile states, this technology does not work well in cooler climates currently. In addition, the energy simulation of thermochromic windows also highlights the fact that this type of glazing is more efficient in warmer climates.

Finally, it should be mentioned that there are a few works contributed to the energy modeling and heat transfer analysis of thermochromic thin films. This can be emphasized in the future attempts.

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